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RADIO-ACTIVITY

OF

URANIUM.

BY

SIR WILLIAM CROOKES, F.R.S., &c.

Read before the Royal Society, May 10, 1900.

LONDON.

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1. THE researches of M. Henri Becquerel have shown that compounds of uranium possess the property now called radio-activity; that is, rays emitted by them affect a sensitive photographic plate through bodies usually considered opaque to light; they discharge an electrometer when brought near it; and they are deflected by a magnet. These rays are now called "Becquerel rays," or "uranic rays."

2. On the discovery by M. and Mdme. Curie of polonium and radium, bodies of enormous radio-active powers, it was suggested that uranium might possibly owe its power to the presence of a small quantity of one of these bodies. But in a paper published in the *Revue Générale des Sciences* for January, 1899, Mdme. Curie says:—"This does not appear probable, for if such were the case different samples of uranium compounds would have very different radio-activities, but in the course of a number of experiments made with various samples of metallic uranium, as well as with oxides and salts from various sources, I have never found any marked difference between the relative activities of the same compound."

In another paper* the same author says that "the property of emitting rays . . . which act on photographic plates is a *specific property of uranium and thorium*." "The physical condition of the metal seems to be of an altogether secondary importance." "Uranium and thorium alone are practically active."

3. When the discovery of radium was announced, and it was said to have "to all appearance the properties of almost pure barium,"† it occurred to me that radium might be found in detectable quantities in some barium minerals were search made among them from different localities. Accordingly specimens of the following minerals were put on sensitive plates, a sheet of black paper separating them from the sensitive surface. As it was probable that the radio-active substance would be present, if at all, in very minute quantities, the sensitive plate was exposed to their influence for forty-eight hours.

* M. and Mdme. Curie, *Comptes Rendus*, vol. cxxvii., p. 175; *Chemical News*, lxxviii., p. 49, July 29, 1898.

† M. and Mdme. Curie and M. Bémont, *Comptes Rendus*, vol. cxxvii., p. 1215; *Chemical News*, lxxix., p. 1, Jan. 3, 1899.

Barytes (Heavy Spar).

- „ from Hungary. (Three specimens).
 - „ „ Cumberland. (Eight).
 - „ „ Westmoreland. (One).
 - „ „ Cumberland. (A fine crystal).
 - „ „ Derbyshire. (Three).
 - „ „ Arkendale. (One).
 - „ „ Hartz. (One).
 - „ „ Scotland. (One).
 - „ „ Ireland. (Two).
 - „ „ Northumberland. (Two).
 - „ „ Arran. (One).
 - „ „ Cherbourg. (One).
 - „ Several unnamed, but finely crystallised, specimens.
- Witherite from Lancashire. (One).**
- „ „ Cumberland. (Four).
 - „ „ Northumberland. (One).

Not one of these minerals showed the slightest action on the sensitive plate.

4. Having obtained negative results with barium compounds, I went through every mineral in my cabinet—a somewhat extensive collection, numbering many fine specimens. Large photographic plates were covered with black paper, and the minerals were laid on them as close as they could conveniently be placed, accurate note of their names and positions being recorded. They were exposed in total darkness for forty-eight hours. By this means a list of radio-active minerals was ultimately obtained. They were then tested for order of intensity of action. The following is a list of active minerals arranged in order, the most active heading the list:—

1. Pitchblende.
2. Uranite.
3. Autunite.
4. Orangite.
5. Thorite.
6. Euxenite.
7. Samarskite.
8. Alvite.
9. Broggerite.
10. Monazite.
11. Xenotime.
12. Arrhenite.
13. Sipilite.
14. Fergusonite.
15. Chalcilite.
16. Hielmite.



FIG. 1.
Photograph taken by daylight of a cut and polished surface of pitchblende.

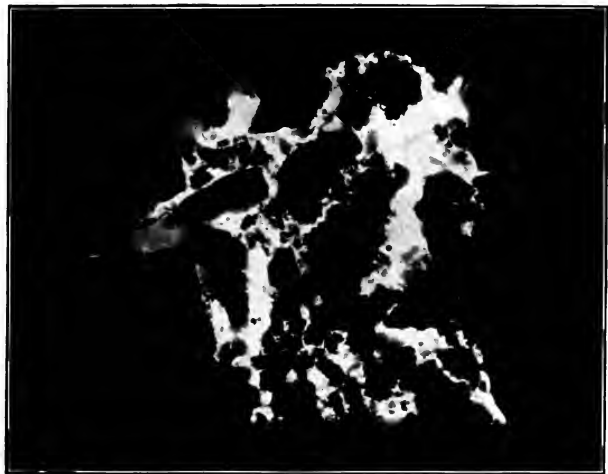


FIG. 2.
Radiograph impressed in the dark by the same surface, showing the portions (white) emitting radiant energy. The luminous parts are pitchblende, the dark parts are felspar, quartz, pyrites, &c. (See Paragraph 5).

It will be observed that these minerals all contain either uranium or thorium.

5. Pitchblende was the most radio-active mineral, but it varied much in different parts. A slice was cut from a piece of pitchblende from Cornwall and the surface was polished. A sensitive photographic plate was pressed against it, and after twenty-four hours the plate was developed. The impression showed the structure of the mineral in a remarkable manner, every little piece of pitchblende showing black, those portions in which the radio-active substance was not so operative showing in half tint, while the felspar, quartz, pyrites, &c., having no radio-activity, left the plate transparent.

Pitchblende from different localities differed greatly in action.

6. A large crystal of orangite from Arendal was ground flat and polished at one end and side, and a piece of sensitive celluloid film, cut half through so as to allow it to bend sharply, was put on the polished surfaces, one half pressing against the end and the other half against the side. The exposure was continued for seventy-two hours. On developing, no difference could be seen in the intensity of the impression, whether made by the end or the side of the crystal. The impression also was uniform over the surface, the cracks in the surfaces not having impressed themselves.

These experiments were repeated with the interposition of a thin sheet of celluloid between the mineral and the sensitive plate. The results were practically the same as before.

7. Roughly speaking, the action of pitchblende is in proportion to the percentage of uranium in the mineral. Finely powdered pitchblende of different degrees of richness were experimented with. Cells were made of thick lead pipes half an inch internal diameter and one inch long, closed at the lower ends with card. They were filled with powdered pitchblende, one containing 43 per cent U_3O_8 and the other 12 per cent U_3O_8 . A sensitive plate being covered with black paper the lead cells were laid on it and kept in total darkness for one hundred and twenty hours. The intensity of the spot under the 43 per cent ore on development was found to be at least three times that of the one under the 12 per cent ore.

Two lead cells were taken, one being a quarter of an inch long and the other two inches long. They were filled completely with the 43 per cent ore, and a sensitive plate exposed to their action for forty-eight hours. On developing it was doubtful whether any difference existed in the intensity of the two spots, proving that the action does not pass

through much thickness of active material, a quarter of an inch being equal in effect to two inches.

No difference in the action was noticed when the bottom of the cell was made of thin glass cemented on, instead of card.

Four cells were filled with pitchblende and placed side by side on a sensitive plate. After having acted twenty-four hours the first was removed, the second after forty-eight hours, the third after seventy-two hours, and the last was kept on for ninety-six hours. On developing the plate the spots had intensities varying with the lengths of exposure, and in about the right proportion, on the assumption that double the time of action gives double the intensity of blackening.

8. For convenience of comparison I had a number of glass cells made, three-quarters of an inch wide and deep, so that they could either be sealed up or closed with a cork. A piece of apparatus was made so as to take radiographs of samples with more ease and certainty. A lead plate, 2 m.m. thick, $6\frac{1}{2}$ inches long, and $2\frac{1}{8}$ inch wide, has circular holes punched in it, one inch in diameter. Under the thick plate of lead is another thinner plate, made of pure assay foil, and having holes in it, concentric with the others, but barely $\frac{3}{4}$ inch in diameter, so that one of the small cells will not pass through the lower hole, but will pass easily through the upper hole, and thus be kept in place. To prevent contact between the lead plate and the sensitive surface a thin sheet of celluloid is fixed beneath, with holes punched in it concentric with those in the lead plates. In the top left corner of the lead plates is a short steel pin, which can be pressed on the sensitive plate and so register its position in respect to the cells experimented with. The lead and celluloid plates are then bound together and the whole is fitted into a shallow wooden tray with a light-tight cover.

A sensitive film is laid face upwards at the bottom of the wooden tray; on this are put the lead screens, and then the experimental cells of radio-active bodies in order, careful note being taken of their relative positions.

9. Wishing to prepare compounds of radium and polonium, the very curious bodies discovered by M. and Mme. Curie, I arranged with my friend Mr. Tyrer, Stirling Chemical Works, for the systematic working up of half a ton of pitchblende. It was necessary to examine every precipitate and filtrate in each stage of the operation, and for convenience of registration they had to be compared with a standard cell filled with a substance unvarying in action. After many

trials I selected crystallised uranium nitrate as being strongly radio-active and easily prepared pure. This led me to the observation which forms the subject of the present paper.

10. The following compounds of uranium were tested simultaneously, being put into glass cells and arranged on a lead screen with seven holes:—

1. Metallic uranium, from M. Moissan.
2. Uranium nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.
3. Uranium acetate.
4. Uranium persulphate.
5. Uranium protosulphate.
6. Uranium oxide (green), UO_2UO_3 .
7. Uranium oxide (black), UO_2UO_3 .

For twenty-four hours the sensitive plate was exposed to the influence of these bodies. With the exception of metallic uranium; which showed least action, there was not much difference between the effect produced by any of the others.

11. In order to prepare uranium nitrate of great purity for a standard I took some pounds of the commercial salt and purified it, first by solution in ether (13) and then by repeated crystallisation. After many operations a cell was filled with the crystals and it was used as a standard. To my surprise, after having acted on a sensitive plate for twenty-four hours, on development not a trace of image could be seen.

12. Thereupon I tried the following experiments to ascertain if the great radio-activity of some uranium compounds and the absence of it in others might be caused by some variation of physical, crystalline, or chemical condition.

Commercial uranium nitrate was taken, and—

(1). A portion was heated with excess of nitric acid to dryness on the water-bath. It was powdered and put in a cell.

(2). A similar portion of the salt was dissolved in alcohol and the solution evaporated to dryness over the water-bath. The resulting orange-coloured pasty material was ground and put in a cell.

(3). The salt was treated in the same way as No. 1, except that the excess of water and acid were not driven off.

(4). A small quantity was heated for some time on a water-bath till it was thoroughly dry. It was then powdered and put in a cell.

(5). 50 grains were put in a glass cell and heated on a water-bath to about 75°C . till it had dissolved in its water of crystallisation.

(6). 50 grains in a glass cell were heated on a sand-bath to about 230°C . The water of crystallisation having been driven off the salt fused, and on cooling remained a hard, yellow, glassy mass.

(7). A similar quantity of the same salt was heated to a little above 230°C . till it commenced to decompose.

(8). A similar quantity was heated more strongly, till about half the nitrate had decomposed.

(9). The same quantity was heated till decomposition was complete.

(10). As a standard, some of the same lot of commercial uranium nitrate from which these lots were taken was put in a cell.

These ten cells were placed in a lead screen apparatus and a sensitive plate was exposed to their influence for twenty-four hours. On development there was not much difference between any of the impressions, that under No. 9 being a little the strongest.

Thus it appears that no modification of physical or chemical condition materially affects the radio-active property of a uranium compound when, to begin with, the salt experimented on possesses it; other similar experiments show that, starting with an inactive uranium salt, nothing that can be done to it will cause it to acquire this property. It is therefore evident that, as I had suspected, the radio-active property ascribed to uranium and its compounds is not an inherent property of the element, but resides in some outside body which can be separated from it.

Having by repeated crystallisation succeeded in preparing a photographically inactive uranium nitrate, I started experiments with several pounds of the commercial salt to ascertain the readiest means of separating from it the active body.

13. Into a stoppered cylinder I put one pound of crystallised nitrate and poured on it a pound of methylated ether, sp. gr. 0.72. The salt easily dissolved on shaking, and after a few hours the whole of the crystals had disappeared, leaving at the bottom of the cylinder 1000 fluid grains of a heavy aqueous solution. I separated the aqueous solution from the ethereal solution, and evaporated it to dryness to remove traces of ether. The ethereal solution was allowed to evaporate spontaneously. Equal quantities of the soluble and the insoluble in ether I put into glass cells and added sufficient dilute nitric acid to dissolve the salt, and then evaporated each lot to dryness on the water-bath. When dry the two cells, and a third containing some of the original nitrate, were put on a sensitive plate for twenty-four hours.

On development it was found that the action of the part undissolved by ether was very strong, that of the original nitrate not more than half as strong, while no action whatever could be detected on the part of the plate covered by the salt soluble in ether,

The portion insoluble in ether, after evaporation to dryness with nitric acid, and then crystallisation in water, in no way differed in appearance from ordinary uranium nitrate. The portion soluble in ether, when dried, heated with dilute nitric acid, and crystallised, also had the same appearance as the initial salt.

14. The crystallised nitrate from the portion insoluble in ether I again extracted with ether. Most of it dissolved, and a small portion of heavy aqueous liquid settled at the bottom. As before, the nitrate which dissolved in ether had scarcely any radio-active power, while the residue from this second extraction possessed it in a strong degree. The residue after the second extraction was about double the activity of the residue after the first extraction, showing that ether, while dissolving uranium nitrate itself with facility, does not dissolve the body to which it owes its radio-activity.

15. The uranium nitrate from the portion insoluble in ether was submitted to fractional crystallisation, in the following manner:—

The solution was evaporated until on cooling about three-fourths would crystallise out. The beaker in which this operation was performed was called No. 1. When crystallisation had finished, the mother-liquor was poured into a beaker called No. 2. A little water was added to No. 1 and it was warmed to dissolve the crystals; No. 2 was evaporated a little, and both were set aside to crystallise. When cold the mother-liquor from 2 was poured into a beaker No. 3, the mother-liquor from 1 was poured into 2, a little water being added to dissolve the crystals in 1, and the contents of the three beakers were warmed and allowed again to crystallise separately. This operation was continued as long as the uranium salt would hold out, or till the tests showed that the operations had gone far enough.

16. Tests were made to see how the operations were proceeding. A portion of the crystals from No. 1 beaker was dried and put into a cell. Some mother-liquor from the last beaker was also evaporated and crystallised, and the crystals were put in a cell. The two were placed side by side on a sensitive plate and the action was allowed to proceed for twenty-four hours. On development there was no visible spot beneath No. 1 nitrate, while that beneath the nitrate

from the other end of the fractionation was strong and black.

17. The crystals were removed from their cells, ignited to the green oxide, and replaced. Tested again on a sensitive plate the results were similar to those given by the unignited nitrates. The active substance, therefore, is seen to reside in the mother-liquor.

18. In making photographic tests it is not necessary to take much of the substance. On an ordinary microscopic slide I put a small drop of liquid from each of the highest five fractionations, Nos. 10, 9, 8, 7, and 6. The drops were allowed to crystallise and the slide was laid on a sensitive plate. In twenty-four hours a good impression of No. 10, the highest fraction, was obtained; a less strong impression of the next, No. 9; a fainter one of 8; a scarcely perceptible one of 7; and no impression at all from No. 6. The slide containing the five crystalline spots was then covered with another glass, and the whole cemented together with Canada balsam and mounted in the manner usual with microscopic slides. When the balsam was dry the slide was put on a sensitive plate. In twenty-four hours a good graduated image was developed.

19. There are in commerce two kinds of uranium nitrate: one, the commercial variety, and another called "purissimum." I am informed that the "purissimum" is prepared from the former by repeated crystallisation. I purchased some of each of these nitrates and tested them on a photographic plate. The commercial variety proved to be at least twice as radio-active as the "purissimum" salt.

20. Experiments were now instituted with a view of obtaining a wholly inactive uranium nitrate. About two pounds of the salt that had been obtained from the solution in ether was repeatedly crystallised, pouring off the mother-liquor each time. This and the next succeeding two lots of crystals (Nos. 1, 2, and 3), were put into cells, and kept on a sensitive plate for seven days. On developing the plate no image could be detected where No. 1 had been; a scarcely perceptible impression could be just detected at No. 2, and a little stronger impression at No. 3.

21. Other methods were attempted for the separation of the active substance from uranium. Uranium nitrate fuses at a moderate temperature, and after some time it becomes darker, and nitrous fumes come off. Finally, the mass becomes semi-fluid, and will not run. The operation is then stopped, and the mass transferred to water; the undecomposed nitrate is dissolved out, leaving an insoluble basic

nitrate. The basic nitrate is of an orange-yellow colour, easily dissolved in nitric acid to again form the normal nitrate. By using this method of fractionation the active body gradually accumulates towards the basic end. But the method is neither so complete nor so easily effected as the crystallisation method, and therefore I have not pushed it very far. I have, however, proved that the radio-activity of nitrate of uranium can be concentrated by fractionation to the basic nitrate end, the nitrate at the other end being diminished in radio-activity.

22. A highly active uranium nitrate, prepared by fractionation from the part insoluble in ether, was dissolved in water, and ammonia in excess was added. Yellow ammonium uranate was precipitated. The filtrate was evaporated to dryness, and heated with nitric acid. The yellow precipitate and the residue of the filtrate were put into cells, and laid on a sensitive plate. After twenty-four hours' action the plate was developed, when it was seen that the whole of the radio-activity resided in the ammonium uranate, the other substance showing nothing. This experiment proves that the active body is precipitated by ammonia, and is insoluble in excess.

23. Another portion of active uranium nitrate was dissolved in water, with an excess of ammonium carbonate. The first formed precipitate almost entirely re-dissolved, leaving a small quantity of insoluble light brown flocculent precipitate. This collected on warming, like alumina. It was filtered off, well washed and dried, and put in a glass cell.

The filtrate from the above precipitate was evaporated to drive off the ammonium carbonate, when a yellow precipitate came down. This was filtered, washed, dried, and put into a cell.

These precipitates were exposed for twenty-four hours in a lead screen apparatus. On developing it was seen that the residue insoluble in ammonium carbonate instantly flashed out black and dense, while the salt precipitated from the ammonium carbonate solution gave a scarcely discernible image.

24. The action of the precipitate insoluble in ammonium carbonate was so strong that another experiment was tried, exposing the sensitive plate to its action for one hour. On development the disk of action came out strong and black, although not so black as in the twenty-four hours experiment. It was now laid for five minutes on a sensitive plate. Here the action was distinct—about as strong as that given

by ordinary uranium nitrate in twenty-four hours. These experiments prove that the active body can exist apart from uranium.

If a sheet of thin glass or celluloid is laid on a sensitive plate, and the dried filter-paper with its contents laid on that, and kept down by a weight, an impression is given in as short a space of time as if a glass cell had been used.

25. The radio-active body is not entirely insoluble in ammonium carbonate. A portion of the very active precipitate left after separation from the uranium was dissolved in dilute hydrochloric acid, and an excess of ammonium carbonate added. The precipitate was very brown, due to the presence of iron. It was dried and tested. The filtrate was well boiled, and as the ammonium carbonate evaporated a slight precipitate came down. This was collected on a filter and tested by the side of the first precipitate. On developing the plate the images produced by each precipitate were of about equal intensity. The brown precipitate was digested in very dilute hydrochloric acid in the cold. The iron partially dissolved before the rest of the substance, leaving the residue decidedly paler in colour. This pale body was just as radio-active as before the partial removal of the iron. Therefore the presence of iron does not interfere with the activity of the substance.

26. Having thus definitely proved that the supposed radio-activity of uranium and its salts is not an inherent property of the element, but is due to the presence of a foreign body,* it is necessary patiently to determine the nature of the foreign body. Several radio-active bodies claimed to be new have already been extracted from pitchblende, and experiments have been instituted to see if the newly found body UrX had similar chemical properties to those of the older active substances.

27. Polonium was first tried. A photographic plate had a thin sheet of celluloid laid on it, and over this a sheet of aluminium foil, 0.05 m.m. thick. On this double layer were put two cells, one containing basic polonium nitrate, the other active UrX. Action was allowed to proceed for twenty-four hours, and the plate was then developed. A disk of blackening was seen under where the UrX stood, the action having passed through the glass, celluloid, and aluminium. Under the polonium nitrate no trace of action could be detected.

* For the sake of lucidity the new body must have a name. Until it is more tractable I will call it provisionally UrX—the unknown substance in uranium.

The experiment was repeated, minus the aluminium foil, and the action continued only two and a-quarter hours. On development, the UrX was found to have acted well, while the polonium showed no trace of action.

28. This behaviour of polonium being excentric or contrary to published accounts,* I put some polonium nitrate in a very thin gelatine capsule, and laid it for eight hours on a sensitive plate. No trace of an image could be seen on development.

The same polonium nitrate was put in a watch-glass, and the sensitive plate put *over it* face downwards, so that it might be exposed to the direct emanations from the polonium nitrate. On the top of the plate was laid a sheet of lead to press it tight to the edges of the watch-glass.

The exposure was continued for twenty-eight hours. On developing a strong action was seen, strongest in the middle where opposed to the thickest part of the heap of polonium nitrate, and weaker towards the edge. A well-marked action took place all over the plate exposed to the interior of the watch-glass, but it was sharply cut off at the edges. This confirms the previous results—that the emanations from polonium are of a different character to those from radium or UrX, both of which pass through glass, aluminium, and lead.

29. Another property of polonium sharply distinguishing it from UrX is volatility. The discoverers first obtained it by subliming pitchblende *in vacuo*. Afterwards they used this property to separate it from bismuth, the polonium and the bismuth sulphides depositing at different parts of the hot tube.

A strongly radio-active compound of UrX was ignited in a blowpipe flame with the addition of a drop of sulphuric acid.

* "The rays emitted by compounds of polonium render barium platinocyanide fluorescent. . . . To make the experiment, place on the active substance a very thin sheet of aluminium, and on this a thin layer of barium platinocyanide; in the dark the barium platinocyanide appears feebly luminous over the active substance."—(M. and Mme. Curie and M. Bémont, *Comptes Rendus*, vol. cxxvii., p. 1215; *Chemical News*, vol. lxxix., p. 1). "Polonic rays act on sensitive plates. The substance we call sulphide of polonium gives a good impression after only three minutes, and there is a decided action noticed after even half a minute."—(Mme. Curie, *Revue Générale des Sciences*, Jan. 30, 1899; *Chemical News*, vol. lxxix., p. 77). In the same paper the authoress, after describing the power possessed by a polonium compound to excite phosphorescence, says: "the rays emitted by this latter body have traversed the aluminium and excited the fluorescence of the platinocyanide above it." It is evident from the above extracts that I was justified in thinking that polonium rays were not entirely stopped by thin aluminium, glass, or celluloid.

Its radio-activity, on a sensitive plate, was not diminished by this treatment. This experiment was tried several times at increasingly higher temperatures, and always with the same result.

30. Polonium is precipitated by sulphuretted hydrogen, in an acid solution. An acid or neutral solution of UrX is not precipitated by this reagent. Therefore I am justified in saying my UrX is not polonium.

31. But it is not so easy to settle whether UrX is distinct from radium, although many arguments point to its not being radium. The discoverers of radium give several of its chemical properties, and in most of these UrX and Ra are entirely different. Thus, radium sulphate is said to be insoluble in water and acids, while UrX dissolves easily to a clear solution in dilute sulphuric acid. Radium salts are said to be not precipitated by ammonium sulphide or by ammonia, while UrX is precipitated by both.

32. It was hoped that doubtful points might be settled conclusively by the spectrum, as both radium and polonium give well-defined and characteristic lines, especially in the ultra-violet part of the spectrum where I have chiefly worked. M. Demarçay* has given a list of some of the principal lines in the radium spectrum between the wave-lengths 3649·6 to 4826·3, the one at 3814·7 being very strong, and those at 4683·0, 4340·6, and 3649·6 being next in intensity. He draws special attention to the line at 3814·7 as the line showing first in a compound poor in radium. In none of my UrX compounds have I been able to detect a trace of this line; on the other hand I have failed to photograph this line in products which I know contain radium. The reason is my radium compound is too weak. M. Demarçay says that the line is scarcely visible with a radium compound only sixty times as active as uranium. My substance containing radium was still weaker, judging from its action on a photographic plate.

33. The same reasoning applies to polonium. With polonium I have obtained strong lines in the ultra-violet, but I can detect none of them in the spectrum of my compound of UrX . All that I can see are lines belonging to—

Platinum (from the poles),
Uranium,
Calcium,
Aluminum,

* *Comptes Rendus*, vol. cxxiv., p. 716; *Chemical News*, vol. lxxx., p. 259.

and a few of the strongest air lines, besides a large number of faint lines difficult to identify.

34. Spectrum experiments having failed to show a difference between radium and UrX, it was thought that possibly some information might be gained by submitting them to the radiant matter test, which has proved so fruitful in its application to the yttrium earths. Some of the most active UrX was put in a tube furnished with a pair of terminals and it was exhausted to a high point, heat being applied during exhaustion. Simultaneously a self-luminous radium compound was sealed in a vacuum tube and exhausted, heat being likewise applied. When fully exhausted a strong induction spark was passed through each tube. The UrX compound phosphoresced of a fine blue colour. In the spectroscope no discontinuity could be seen in the spectrum of the phosphorescent light.

Under the influence of the induction spark, the radium compound phosphoresced of a luminous rose-colour, showing in the spectroscope a concentration of light in the red-orange and a very faint citron band, due to a trace of yttrium, probably an impurity.

35. A powerful radium compound and one of UrX each in a glass cell, and a paper tray full of polonium sub-nitrate, were placed side by side and a strip of white card was put as a reflector at the back. In front a photographic camera was arranged so as to throw full sized images of the polonium, UrX, and radium compounds on a sensitive plate, and the whole was kept in total darkness for five days. On development the image of the radium with the containing bottles was visible, but not a trace of image from the polonium could be seen. This confirms previous observations that the radiations from polonium will not pass through glass. Those from radium and UrX easily penetrate glass and other media (28).

36. Recently claims have been put forward for the existence of a third radio-active body in pitchblende. In the *Comptes Rendus* for October 16, 1899, and April 2, 1900, M. A. Debierne describes a radio-active body to which he gives the name of "Actinium." At first he said "actinium" showed the principal analytical properties of titanium, but later he describes it as not resembling titanium in all its reactions. M. Debierne gives many reactions of the new substance, and in some instances they are like those of radium. But he qualifies them by the statement that they cannot yet be considered as belonging definitely to the new radio-active substance because up to the present it has not been obtained

sufficiently concentrated. He believes rather that these reactions should be looked upon as the result of retention, analogous to that of iron oxide by barium sulphate. He says that the chemical reactions of the most active substance which he obtained, together with its spectroscopic examination, showed that it chiefly consists of thorium. He cannot, however, be sure that it resembles thorium in all its reactions.

37. Experiments have been commenced to see if it is possible to separate thorium compounds into an active and an inactive body. A strong solution of thorium sulphate was slightly acidulated with sulphuric acid, and gradually raised to the boiling point. A copious precipitate of sulphate came down and was filtered hot. The precipitate was dissolved in cold water and the solution re-heated, when a precipitation of the sulphate again occurred. The mother-liquor from one crystallisation was added to the crystals from another in the systematic manner adopted in fractionation, and when the operations had proceeded some time a test was made on the "head" and "tail." A small quantity of solution from each was evaporated to dryness and strongly ignited before the blowpipe. The two lots of earth were put in cells and a sensitive plate exposed to their action for seventy-two hours. On development not the slightest difference could be detected between the impressions produced by either of the fractions.

I next tried partial crystallisation of thorium nitrate, fractionating it in the way already described in the case of uranium (15). Great difficulties were here encountered, owing to the tendency of a strong solution of thorium nitrate to remain supersaturated for several days, when it would suddenly crystallise to a solid mass. After some weeks, however, six fractionations were effected, and tests were made on the first and last of the series.

The sensitive plate was exposed to their action for one hundred and twenty hours. On development, the fraction at the first end (crystals) gave a very feeble action, while that at the other end (mother-liquors) gave an impression about three times as intense. This points to the possibility of separating from thorium its radio-active substance.

By the kindness of Dr. Knöfler, of Berlin, who makes thorium nitrate by the ton, I have at my disposal some specially prepared thorium nitrate, which is chemically pure. Thoria prepared from this, tested on a sensitive plate, gave a feeble impression in one hundred and twenty hours.

38. In the present state of our knowledge of these radio-active bodies it is safest to retain an open, or even a slightly sceptical mind. We recognise them mainly by the photographic and the electrical tests—reactions which are so sensitive that they give strong results, even when the active body is present in too small a quantity to be detected by its spectrum—one of the most delicate of tests. Knowing the tendency of ordinary chemical bodies to be carried down when a precipitate is formed in their presence, even when no question of sparse solubility is involved, it is not surprising that radium and actinium, to say nothing of UrX, appear to simulate elements which may ultimately prove to be very different from them in chemical characters. For instance, UrX dissolves easily in dilute sulphuric acid, and, I have reason to believe, forms a soluble sulphate; still, when chloride of barium is mixed with it and precipitated as a sulphate, I invariably find strong radio-activity in the precipitated sulphate as well as in the filtrate from the barium sulphate.

To adduce a simile from my previous researches, the first surmises as to the chemical characteristics of the bodies now known to be yttrium and samarium, were widely different from reality. The differences were entirely due to the perturbing cause which is active in the present case—the tendency of the bodies to be carried down and entangled in precipitates, where, according to ordinary chemical laws, they ought not to occur; and to the extreme delicacy of the radiant matter test, which in the case of samarium detects one part in $2\frac{1}{2}$ million parts of calcium, and in the case of yttrium detects one part in the presence of a million parts of extraneous matter.

39. The radiographic test for these active bodies presents another point to be borne in mind. Other tests for the presence of an element either act quickly, or do not act at all, with a comparatively narrow margin of debatable land where the indications of the test may be doubtful. Here, however, the test is cumulative. Like an astronomer photographing stars too faint for his telescope to disclose, he has only to expose the plate for a sufficiently long time and the star reveals itself on development. So, in the case of radio-active minerals or precipitates, if no action is apparent at the end of an hour, one may be shown after twenty-four hours. If a day's exposure will show nothing, try a week's. Considering my most active UrX does not contain sufficient of the real material to show in the spectrograph, yet is powerful enough to give a good impression on a photo-

graphic plate in five minutes, what must be its dilution in compounds which require an hour, a day, or a week to give an action ?



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